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(54) Title: THERMAL DIGITAL LITHOGRAPHIC PRINTING PLATE

(57) Abstract: A thermally imageable element, useful as a lithographic printing plate precursor is disclosed. The element comprises a hydrophilic substrate; an underlayer comprising a first polymeric material; and an ink-receptive top layer comprising a second polymeric material and a solubility-suppressing component. The solubility-suppressing component may be a separate dissolution inhibitor compound and/or the second polymeric material may also function as a solubility-suppressing component. On thermal exposure the exposed regions of the top layer becomes more readily soluble in an aqueous developer, allowing the developer to remove the top layer and reveal the surface of the hydrophilic substrate. The lithographic printing plate thus formed has excellent properties, including the absence of sludging of the developer.



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TITLE
THERMAL DIGITAL LITHOGRAPHIC PRINTING PLATE

FIELD OF THE INVENTION

5 The invention relates to multilayer thermally imageable elements useful in lithographic printing. More particularly, this invention relates to lithographic printing plates that can be thermally imaged by imagewise exposure with a laser or a thermal printing head.

BACKGROUND OF THE INVENTION

10 In lithographic printing, ink receptive areas are generated on the surface of a hydrophilic surface. When the surface is moistened with water and ink is applied, the hydrophilic regions retain the water and repel the ink and the ink receptive areas accept the ink and repel the water. The ink is transferred to the surface of a material upon
15 which the image is to be reproduced. Typically, the ink is first transferred to an intermediate blanket, which in turn transfers the ink to the surface of the material upon which the image is to be reproduced.

 Lithographic printing plates typically comprise a radiation-sensitive coating applied over the hydrophilic surface of a support. If after exposure to radiation the
20 exposed regions of the coating become soluble and are removed in the developing process revealing the underlying hydrophilic surface of the support, the plate is called as a positive-working printing plate. Conversely, if exposed regions of the plate become insoluble in the developer and the unexposed regions are removed by the developing process, the plate is called a negative-working plate. In each instance, the regions of the
25 radiation-sensitive layer (*i.e.*, the image areas) that remain are ink-receptive and the regions of the hydrophilic surface revealed by developing process accept water, a typically fountain solution, and repel ink.

 Direct digital imaging of offset printing plates, which obviates the need for exposure through a negative, is becoming increasingly important in the printing
30 industry. Heat-sensitive imaging elements for the preparation of positive-working lithographic printing plates have been disclosed that comprise a substrate, an aqueous alkali soluble underlayer, and an infrared sensitive top layer. After infrared exposure,

the exposed regions of the top layer are removable with an aqueous alkaline developer, revealing the underlying substrate. Imaging can be carried out with an infrared laser.

Thermally imageable systems have been developed in which it is believed that a thermally frangible complex is formed between a polymeric material and a solubility-suppressing component, which reversibly suppresses the solubility of the polymeric material in the developer. The solubility-suppressing component can be a separate dissolution inhibitor compound and/or the polymeric material can act as a solubility-suppressing component. After imagewise thermal exposure, the rate of dissolution of the exposed regions is greater than the rate of dissolution of the unexposed regions. The exposed regions may be removed by the developer to form an image. Such systems are disclosed in, for example, Parsons, WO 97/39894; Nagasaka, EP 0 823 327; Miyake, EP 0 909 627; West, WO 98/42507; and Nguyen, WO 99/11458.

These systems have limited shelf life and can only be used with a restricted group of developers. They have only a narrow working latitude compared to conventional positive-working printing plates. These systems also have limited resistance to aggressive blanket washes, such as a UV wash.

Systems have been produced in which a developer-insoluble top layer is coated over a developer-soluble underlayer. After exposure the top layer becomes permeable to developer, which penetrates the top layer and dissolves the underlayer, revealing the hydrophilic substrate. However, the developer insoluble material in the top layer, which is removed when the underlayer is removed, causes sludging in the developer. Insoluble particles, which can adhere to the imaged and developed printing plate and adversely affect the quality of the printed image, are produced. The processor must be modified so that the insoluble particles are not circulated in the developer. Thus, a need exists for an improved thermally imageable element that does not suffer from these disadvantages.

SUMMARY OF THE INVENTION

The invention is a multilayer thermally imageable element. The element comprises, in order:

- a) a substrate, the substrate having a hydrophilic surface;
- b) an underlayer over the hydrophilic surface, the underlayer comprising a first polymeric material; and

c) a top layer over the underlayer, the top layer comprising a second polymeric material;

in which:

the top layer is ink receptive;

5 the top layer is insoluble in aqueous alkaline developer;

the top layer comprises at least one solubility-suppressing component;

the underlayer comprises a photothermal conversion material;

the underlayer is soluble in aqueous alkaline developer; and

the second polymeric material is soluble in aqueous alkaline developer.

10 The top layer is insoluble in an aqueous alkaline developer before thermal exposure but becomes removable by the aqueous alkaline developer following thermal exposure.

In a preferred embodiment, the top layer comprises a solubility-suppressing component and the second polymeric material contains phenolic hydroxyl groups. The
15 solubility-suppressing component may be a dissolution inhibitor compound and/or the second polymeric material may act as the solubility-suppressing component. Novolac resins functionalized with sulfonate ester groups are preferred polymeric materials that function as solubility-suppressing components. Quinonediazides (*i.e.*, compounds that contain the *o*-diazonaphthoquinone moiety) are preferred dissolution inhibitor
20 compounds.

In another preferred embodiment, the underlayer comprises an absorber than absorbs radiation in the range of the imaging wavelength, typically about 800 nm to 1200 nm. In another preferred embodiment the underlayer comprises a solvent resistant underlayer or a negative-working, base soluble photosensitive composition. In another
25 embodiment, the invention is an exposed and developed element, which can be used as a lithographic printing member. In another embodiment, the invention is a process for forming the lithographic printing member. In still another embodiment, the invention is a method of printing using the lithographic printing member.

30 DETAILED DESCRIPTION OF THE INVENTION

The thermally imageable element (sometimes referred to as a printing plate precursor) comprises a hydrophilic substrate, typically comprising an aluminum or

polyester support; a radiation absorbing underlayer comprising a first polymeric material; and an ink-receptive top layer comprising a second polymeric material. Although other layers, such as radiation absorbing layers may be present, typically no other layers are present.

5 The top layer preferably comprises a compound that functions as a solubility-suppressing component. The solubility-suppressing component may be a separate dissolution inhibitor compound and/or the second polymeric material may also function as a solubility-suppressing component. Following exposure to radiation, top layer becomes more readily removable by an aqueous alkaline developer, *i.e.*, more soluble or
10 more readily dispersible in the aqueous alkaline developer. The aqueous alkaline developer removes the top layer and reveals the hydrophilic surface of the substrate in the exposed regions. The lithographic printing member thus formed has excellent properties, including the absence of sludging of the developer.

Hydrophilic Substrate

15 The hydrophilic substrate, *i.e.*, the substrate that comprises at least one hydrophilic surface, comprises a support, which may be any material conventionally used to prepare lithographic printing plates. The support is preferably strong, stable and flexible. It should resist dimensional change under conditions of use so that color records will register in a full-color image. Typically, it can be any self-supporting
20 material, including polymeric films, ceramics, metals, or stiff papers, or a lamination of any of these materials. Paper supports are typically "saturated" with polymeric to impart water resistance, dimensional stability and strength.

 Metal supports include aluminum, zinc, titanium, and alloys thereof. A preferred metal support is an aluminum sheet. The surface of the aluminum sheet may be treated
25 by techniques known in the art, including physical graining, electrochemical graining, chemical graining, and anodizing, and then conditioned by chemical means, for example by treatment with water, a solution of phosphate or silicate salt, or a polycarboxylic acid to produce the hydrophilic surface.

 If the surface is roughened, the average roughness R_a is preferably in the range
30 $0.1\ \mu\text{m}$ to $0.8\ \mu\text{m}$. Roughened substrates in which the surface has a surface roughness of $0.1\ \mu\text{m}$ to $2\ \mu\text{m}$ are disclosed in Bhambra, WO97/19819 (PCT/GB96/02883); Bhambra, WO98/52769 (PCT/GB98/01500); and Bhambra, WO98/52768

(PCT/GB/98/01496). In these substrates the support is coated with a hydrophilic layer that comprises a mixture of two particulate materials, preferably alumina and titanium dioxide. The mean particle size of the alumina particles is preferably in the range of 1 μm to 5 μm ; the mean particle size of the titanium dioxide particles is preferably in the
5 range of 0.1 μm to 0.5 μm .

Useful polymeric films include polyester films, such as MYLAR® polyethylene terephthalate film (DuPont., Wilmington, DE), and polyethylene naphthanate. A preferred polymeric film is polyethylene terephthalate.

The substrate may consist only of the support, or it may additionally comprise
10 one or more optional subbing and/or adhesion layers. Typically, polymeric films contain a sub-coating on one or both surfaces to modify the surface characteristics to enhance the hydrophilicity of the surface, to improve adhesion to subsequent layers, to improve planarity of paper substrates, and the like. The nature of this layer or layers depends upon the substrate and the composition of subsequent coated layers. Examples
15 of subbing layer materials are adhesion-promoting materials, such as alkoxysilanes, aminopropyltriethoxysilane, glycidoxypentyltriethoxysilane and epoxy functional polymers, as well as conventional subbing materials used on polyester bases in photographic films.

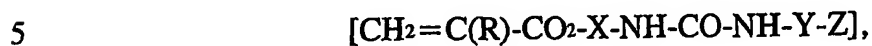
The back side of the substrate (*i.e.*, the side opposite the underlayer and top
20 layer) may be coated with an antistatic agent and/or a slipping layer or matte layer to improve handling and "feel" of the imageable element.

The support should be of sufficient thickness to sustain the wear from printing and be thin enough to wrap around a printing form. Polyethylene terephthalate or polyethylene naphthanate, typically has a thickness of from about 100 to about 310 μm ,
25 preferably about 175 μm . Aluminum sheet typically has a thickness of from about 100 to about 600 μm .

Underlayer

The underlayer, or first layer, is over the hydrophilic surface of the hydrophilic substrate. After imaging, it is removed by the aqueous alkaline developer to expose the
30 underlying hydrophilic surface of the substrate. It is preferably soluble in the aqueous alkaline developer to prevent sludging of the developer. Preferably it is soluble in a wholly aqueous developer, *i.e.* one that does not include added organic solvents.

urea bond in its side chain (*i.e.*, a pendent urea group), such are disclosed in Ishizuka, U.S. Pat. No. 5,731,127. These copolymers comprise about 10 to 80 wt%, preferably about 20 to 80 wt%, of one of more monomers represented by the general formula:



in which R is -H or -CH₃; X is a bivalent linking group; Y is a substituted or unsubstituted bivalent aromatic group; and Z is -OH, -COOH, or -SO₂NH₂.

R is -preferably CH₃. Preferably X is a substituted or unsubstituted alkylene
10 group, substituted or unsubstituted phenylene [C₆H₄] group, or substituted or unsubstituted naphthalene [C₁₀H₆] group; such as -(CH₂)_n-, in which n is 2 to 8; 1,2-, 1,3-, and 1,4-phenylene; and 1,4-, 2,7-, and 1,8-naphthalene. More preferably X is unsubstituted and even more preferably n is 2 or 3; most preferably X is -(CH₂CH₂)-. Preferably Y is
15 a substituted or unsubstituted phenylene group or substituted or unsubstituted naphthalene group; such as 1,2-, 1,3-, and 1,4-phenylene; and 1,4-, 2,7-, and 1,8-naphthalene. More preferably Y is unsubstituted, most preferably unsubstituted 1,4-phenylene. Z is -OH, -COOH, or -SO₂NH₂, preferably -OH. A preferred monomer is:



in which Z is -OH, -COOH, or -SO₂NH₂, preferably -OH.

In the synthesis of a copolymer, one or more of the urea group containing monomers may be used. The copolymers also comprise 20 to 90 wt% other
polymerizable monomers, such as maleimide, acrylic acid, methacrylic acid, acrylic
25 esters, methacrylic esters, acrylonitrile, methacrylonitrile, acrylamides, and methacrylamides. A copolymer that comprises in excess of 60 mol% and not more than 90 mol% of acrylonitrile and/or methacrylonitrile in addition to acrylamide and/or methacrylamide provides superior physical properties. More preferably the alkaline soluble copolymers comprise 30 to 70 wt% urea group containing monomer; 20 to 60 wt% acrylonitrile or
30 methacrylonitrile, preferably acrylonitrile; and 5 to 25 wt% acrylamide or methacrylamide, preferably methacrylamide. These polymeric materials are typically resistant to washes with 80 wt% 2-butoxyethanol/20 wt% water.

The polymeric materials described above are soluble in aqueous alkaline developers. In addition, they are soluble in polar solvents, such as ethylene glycol

monomethyl ether, which can be used as the coating solvent for the underlayer. However, they are poorly soluble in less polar solvents, such as 2-butanone (methyl ethyl ketone), which can be used as a solvent to coat the top layer over the underlayer without dissolving the underlayer.

5 Both these groups of polymeric materials can be prepared by methods, such as free radical polymerization, well known to those skilled in the art. Synthesis of the aqueous alkaline soluble copolymers that have urea bonds in their side chains is disclosed, for example, in Ishizuka, U.S. Pat. No. 5,731,127.

Other aqueous alkaline developer soluble polymeric materials may be useful in
10 the underlayer. Derivatives of methyl vinyl ether/maleic anhydride copolymers that contain an N-substituted cyclic imide moiety and derivatives of styrene/maleic anhydride copolymers that contain an N-substituted cyclic imide moiety may be useful if they have the required solubility characteristics. These copolymers can be prepared by reaction of the maleic anhydride copolymer with an amine, such as *p*-aminobenzenesulfonamide, or
15 *p*-aminophenol, followed by ring closure by acid.

Another group of polymeric materials that are useful in the underlayer include aqueous alkaline developer soluble copolymers that comprise about 10 to 90 mol% of a sulfonamide monomer unit, especially those that comprise N-(*p*-aminosulfonylphenyl)-methacrylamide, N-(*m*-aminosulfonylphenyl)methacrylamide N-(*o*-aminosulfonyl-
20 phenyl)methacrylamide, and/or the corresponding acrylamide. Useful alkaline developer soluble polymeric materials that comprise a pendent sulfonamide group, their method of preparation, and monomers useful for their preparation, are disclosed in Aoshima, U.S. Pat. No. 5,141,838. Particularly useful polymeric materials comprise (1) the sulfonamide monomer unit, especially N-(*p*-aminosulfonylphenyl)methacrylamide; (2) acrylonitrile and/or methacrylonitrile; and (3) methyl methacrylate and/or methyl acrylate.
25 These polymeric materials are typically resistant to washes with 80 wt% 2-butoxyethanol/20 wt% water.

Combinations of alkaline developer soluble polymeric materials may be used in the underlayer to provide improved chemical resistance, *i.e.*, resistance to both fountain
30 solution and to aggressive washes. A combination of a polymeric material that is resistant to 80 wt% diacetone alcohol/20 wt% water, which tests resistance to a UV wash, with a polymeric material that is resistant to 80 wt% 2-butoxyethanol/20 wt%

water, which tests resistance to alcohol sub fountain solution, surprisingly produces a layer that shows good resistance to both solvent mixtures. Preferably, the first polymeric material has a one-minute soak loss of less than about 20%, more preferably less than about 10%, and most preferably less than about 5% in 80 wt% diacetone alcohol/20 wt% water, and the second polymeric material has a one-minute soak loss of less than about 20%, more preferably less than about 10%, and most preferably less than about 10%, in 80 wt% 2-butoxyethanol/20 wt% water. One-minute soak loss is measured by coating a layer of the polymeric material on a substrate, typically at a coating weight of about 1.5 g/m², soaking the coated substrate in the appropriate solvent for one minute at room temperature, drying the coated substrate, and measuring the weight loss as a percent of the total weight of polymeric material present on the substrate.

The ability of an underlayer to withstand both fountain solution and aggressive washes can be estimated by a chemical resistance parameter (CRP), defined as follows:

$$CRP = [(100 - a)(100 - b)]/10^4$$

in which:

a is the one minute % soak loss in 80 wt% diacetone alcohol/20 wt% water; and
b is the one minute % soak loss in 80 wt% 2-butoxyethanol/20 wt% water.

The chemical resistance parameter should be greater than about 0.4, preferably greater than about 0.5, more preferably greater than about 0.6. In favorable cases a chemical resistance parameter of at least about 0.65 can be obtained. The one-minute soak loss in each solvent should be less than about 60%, preferably less than about 40%, and more preferably less than about 35%. Preferably, the one-minute soak loss should be less than about 60%, preferably less than about 40%, and more preferably less than about 35%, in one solvent and less than about 40%, more preferably less than about 30%; and more preferably less than about 20%, and most preferably less than about 10% in the other solvent.

Combination of (1) a copolymer that comprises N-substituted maleimides, especially N-phenylmaleimide; methacrylamides, especially methacrylamide; and acrylic and/or methacrylic acid, especially methacrylic acid (2) with an alkaline soluble copolymer that comprises a urea in its side chain or with an alkaline soluble copolymer

that comprises 10 to 90 mol% of a sulfonamide monomer unit, especially one that comprise N-(*p*-aminosulfonylphenyl)methacrylamide, N-(*m*-aminosulfonylphenyl)-methacrylamide N-(*o*-aminosulfonylphenyl)methacrylamide, and/or the corresponding acrylamide, is especially advantageous. One or more other polymeric materials, such as
5 novolac resins, may also be present in the combination. Preferred other polymeric materials, when present, are novolac resins.

When a combination of polymeric materials is used, the underlayer typically comprises about 10% to about 90% by weight of the polymeric material that is resistant to 80 wt% diacetone alcohol/20 wt% water, and about 10% to about 90% by weight of
10 the polymeric material that is resistant to 80 wt% 2-butoxyethanol/20 wt% water, based on the total weight these polymeric materials in the underlayer. Preferably the underlayer comprises about 40% to about 85% by weight of the polymeric material that is resistant to 80 wt% diacetone alcohol/20 wt% water and about 15% to about 60% of the polymeric material that is resistant to 80 wt% 2-butoxyethanol/20 wt% water, based
15 on the total weight the first and second polymeric materials in the underlayer. The first and second polymeric materials together typically comprise at least about 50 wt%, preferably at least about 60 wt%, and more preferably at least about 65 wt%, of the underlayer, based on total weight of the materials in the underlayer. Up to about 20 wt%, preferably about 1 to about 20 wt%, of other polymeric materials may be present
20 in the underlayer, based on the total amount of all the polymeric materials in the underlayer.

Negative-Working, Base Soluble Photosensitive Compositions

The underlayer may comprise a negative-working, base soluble photosensitive composition. Such compositions are often referred to as "photohardenable
25 compositions" or "photoinsolubilizable compositions" because they become developer insoluble on irradiation. Typically these compositions comprise materials that undergo photocrosslinking, photodimerization, and/or photopolymerization on exposure to actinic radiation, typically ultraviolet light. Photohardenable compositions produce printing plates with high press life and resistance to press room chemicals. Negative working
30 systems are discussed, for example, in Chapter 2 of Photoreactive Polymers: the Science and Technology of Resists, A. Reiser, Wiley, New York, 1989, pp. 22-64.

The underlayer may comprise a negative-working diazonium-containing

composition. Typically the diazonium containing compound is a diazonium polycondensation product. Diazonium polycondensation products well known to those skilled in the art. They may be prepared, for example, by condensation of a diazo monomer, such as is described in Toyama, U.S. Pat. No. 4,687,727 with a condensation agent, such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde or benzaldehyde. Furthermore, mixed condensation products are used which, apart from the diazonium salt units, comprise other non-photosensitive units which are derived from condensable compounds, in particular from aromatic amines, phenols, phenol ethers, aromatic thioethers, aromatic hydrocarbons, aromatic heterocycles or organic acid amides. Especially advantageous examples of diazonium polycondensation products are reaction products of diphenylamine-4-diazonium salts, optionally having a methoxy group in the phenyl group bearing the diazo group, with formaldehyde or 4,4'-bis-methoxymethyl diphenyl ether. Aromatic sulfonates such as 4-tolylsulfonate or mesitylene sulfonate, tetrafluoroborate, hexafluorophosphate, hexafluoroantimonate and hexafluoroarsenate are particularly suitable as anions of these diazo resins. The diazonium polycondensation product is preferably present in the photosensitive mixtures in an amount of from 3 to 60 wt%.

Numerous binders are known. One such system is described in Baumann, U.S. Pat. No. 5,700,619. The binder is an acetalized polyvinyl alcohol, with pendent carboxyl groups.

The underlayer may comprise a photopolymerizable composition. Preferred photosensitive compositions are photopolymerizable compositions, which comprise one or more monomers, one or more binders, and one or more photoinitiator systems. Other components conventionally added to photopolymerizable compositions can be present to modify the physical properties of the film. Such components include: for example, plasticizers, thermal stabilizers, adhesion modifiers, coating aids, and release agents. Nonionic surfactants, for example, may be added to the photopolymerizable composition as coating aids. Such systems are well known in art, and are discussed, for example, in *Photopolymers: Radiation Curable Imaging Systems*, B. M. Monroe in Radiation Curing: Science and Technology, S. P. Pappas, Ed., Plenum, New York, 1992, pp. 399-440.

Photopolymerizable compositions comprise at least one ethylenically unsaturated

compound that undergoes free-radical initiated polymerization, generally known as a monomer. The monomers are typically multifunctional, *i.e.*, they comprise more than one ethylenically unsaturated, free radical polymerizable group. Typical multifunctional monomers are unsaturated esters of alcohols, preferably acrylate and methacrylate esters of polyols, such as, trimethylolpropane triacrylate and trimethacrylate, pentaerythritol triacrylate and trimethacrylate, pentaerythritol tetraacrylate and tetramethacrylate, ethoxylated-trimethylolpropane triacrylate and trimethacrylate, glycerolpropoxy triacrylate and trimethacrylate, ethyleneglycol diacrylate and dimethacrylate, tri-propyleneglycol diacrylate and dimethacrylate, and tetraethyleneglycol diacrylate and dimethacrylate. Oligomers and/or prepolymers, such as urethane acrylate and methacrylate, epoxide acrylate and methacrylate, polyester acrylate and methacrylate, polyether acrylate and methacrylate or unsaturated polyester resins, may also be used. Numerous other unsaturated monomers polymerizable by free-radical initiated polymerization and useful in photopolymerizable compositions are known to those skilled in the art.

The composition comprises at least one preformed macromolecular polymeric material, generally known as a binder. In general, the binder should be soluble or swellable in the coating solvent and compatible with the other components of the photopolymerizable system. Representative binders are poly(methyl methacrylate) and copolymers of methyl methacrylate with other alkyl acrylates, alkyl methacrylates, methacrylic acid, and/or acrylic acid. Numerous other binders useful in photopolymerizable compositions are known to those skilled in the art.

When the material is to be cured by irradiation with ultraviolet or visible radiation, a free radical generating, initiating system activatable by ultraviolet or visible radiation, known as a photoinitiating system, may be present to facilitate polymerization of the polymerizable monomers. The photoinitiator system absorbs in ultraviolet and/or visible regions of the spectrum, *i.e.*, in the range of from 300 to 800 nm, preferably in the ultraviolet, *i.e.* 300 nm to 400 nm.

The photoinitiating system may be a single compound or a mixture of compounds. Suitable photoinitiating systems are disclosed in "Photoinitiators for Free-Radical-Initiated Photoimaging Systems," by B. M. Monroe and G. C. Weed, Chem. Rev., 93, 435-448 (1993) and in "Free Radical Polymerization" by K. K. Dietliker, in

Typical free radical photoinitiating compounds include benzophenone; 2-hydroxy-2-methyl-1-phenylpropan-1-one (Darocur® 1173); 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (Lucerin® TPO); 2,2-dimethoxy-2-phenyl-acetophenone (benzildimethyl ketal, BDK, Irgacure® 651, Lucerin® BDK); 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1 (Irgacure® 907); 1-hydroxycyclohexylphenyl ketone (HCPK, Irgacure® 184); bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl-pentylphosphine oxide; and combinations thereof. Mixed photoinitiators include a 50:50 mixture of 2-hydroxy-2-methyl-1-phenylpropan-1-one and 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (Darocur® 4265); and a 25:75 mixture of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl-pentyl-phosphine oxide and 2-hydroxy-2-methyl-1-phenylpropan-1-one (CGI 1700).

A hybrid system comprising a combination of a diazonium polycondensation product and a free polymerizable system may be advantageous for certain applications. The compositions of such hybrid systems preferably comprise 1 to 50% diazonium polycondensation products, 0.5 to 20% photoinitiators as well as 5 to 80% free radical polymerizable components.

Photocrosslinkable systems typically comprise at least one binder and a photoactivated at least bifunctional crosslinking agent that crosslinks the binder on irradiation. Organic azides, which are believed to form nitrenes on irradiation, have been used to crosslink binders. Diazido compounds, such as the disulfonated derivative of 4,4'-diazidostilbene, are preferred azides for photocrosslinking.

Photodimerizable systems comprise a binder that forms a crosslink on irradiation. Photocrosslinkable binders include, for example, the polyvinyl alcohols functionalized with N-alkyl styrylpyridinium or N-alkyl styrylquinolinium groups, such as are described in, for example, Ichimura, U.S. Pat. Nos. 4,272,620; 4,287,335; 4,339,524; 4,564,580; and 4,777,114.

Photothermal Conversion Material

The underlayer absorbs radiation, preferably radiation in the range of about 800 nm to 1200 nm, the range of radiation commonly used for imaging thermally imageable elements. An absorber, sometimes referred to as "a photothermal conversion material" is present in the underlayer. Photothermal conversion materials absorb radiation and

insoluble in aqueous alkaline developer prior to imaging, but becomes soluble in aqueous alkaline developer following imaging. Second polymeric materials that are water insoluble, but dissolve in an aqueous alkaline developer, are used to prevent sludging of the developer. Typically the underlayer absorbs imaging radiation, *i.e.*,
5 infrared radiation and radiation in the range of 600 nm to 1200 nm, especially in the range of 800 nm to 1200 nm, and the top layer does not substantially absorb imaging radiation, *i.e.*, infrared radiation and radiation in the range of 600 nm to 1200 nm, especially in the range of 800 nm to 1200 nm.

Polymers that contain phenolic hydroxyl groups, *i.e.*, phenolic resins, are
10 preferred. Preferably the polymeric material is a light-stable, water-insoluble, aqueous alkaline developer-soluble, film-forming polymeric material that has a multiplicity of phenolic hydroxyl groups, either on the polymer backbone or on pendant groups. Phenolic groups impart aqueous alkaline developer solubility to the top layer and are also believed to form a thermally frangible complex with the solubility-suppressing
15 component. Novolac resins, resol resins, acrylic resins that contain pendent phenol groups, and polyvinyl phenol resins are preferred phenolic resins. Novolac resins are more preferred.

Novolac resins are commercially available and are well known to those skilled in the art. They are typically prepared by the condensation reaction of a phenol, such as
20 phenol, *m*-cresol, *o*-cresol, *p*-cresol, etc, with an aldehyde, such as formaldehyde, paraformaldehyde, acetaldehyde, etc. or ketone, such as acetone, in the presence of an acid catalyst. The weight average molecular weight is typically about 1,000 to 15,000. Typical novolac resins include, for example, phenol-formaldehyde resins, cresol-formaldehyde resins, phenol-cresol-formaldehyde resins, *p-t*-butylphenol-formaldehyde
25 resins, and pyrogallol-acetone resins. Particularly useful novolac resins are prepared by reacting *m*-cresol, mixtures of *m*-cresol and *p*-cresol, or phenol with formaldehyde using conventional conditions.

Other useful phenolic resins include polyvinyl compounds having phenolic hydroxyl groups. Such compounds include, for example, polyhydroxystyrenes and
30 copolymers containing recurring units of a hydroxystyrene, and polymers and copolymers containing recurring units of substituted hydroxystyrenes.

The top layer preferably comprises a compound that functions as a solubility-

suppressing component for the second polymeric material. While not being bound by any theory or explanation, it is believed that solubility-suppressing components are "reversible insolubilizers," *i.e.*, compounds that reversibly suppress the solubility of the second polymeric material in the aqueous alkaline developer. Solubility-suppressing components have polar functional groups that are believed to act as acceptor sites for hydrogen bonding with the hydroxyl groups present in the second polymeric material. The acceptor sites comprise atoms with high electron density, preferably selected from electronegative first row elements, especially carbon, nitrogen, and oxygen. Solubility-suppressing components that are soluble in the aqueous alkaline developer are preferred.

10 The solubility-suppressing component may be a separate dissolution inhibitor compound. Alternatively, or additionally, the polymeric material may contain polar groups in addition to phenolic groups and, thus, function as both the polymeric material and the solubility-suppressing component. Useful dissolution inhibitor compounds are disclosed in West, U.S. Patent 5,705,308; Bennett, WO97/07986 [PCT/GB96/01973],
15 Nagasaka, EP 0,823,327, and West, U.S. Pat. No. 6,060,222.

 Solubility-suppressing components are believed to reversibly reduce the rate at which the second polymeric material dissolves in an aqueous alkaline developer. In general, such compounds should have an "inhibition factor" of at least 0.5, and preferably at least 5. Inhibition factors for given compounds can be readily measured
20 using the procedure described by Shih *et al*, Macromolecules, 27, 3330 (1994). The inhibition factor is the slope of the line obtained by plotting the log of the development rate as a function of inhibitor concentration in the coating. Development rates are conveniently measured by laser interferometry, as described by Meyerhofer, IEEE Trans. Electron Devices, ED-27, 921 (1980).

25 Useful polar groups include, for example, diazo groups; diazonium groups; keto groups; sulfonic acid ester groups; phosphate esters groups; triarylmethane groups; onium groups, such as sulfonium, iodonium, and phosphonium; groups in which a nitrogen atom is incorporated into a heterocyclic ring; and groups that contain a positively charged atom, especially a positively charged nitrogen atom, typically a
30 quaternized nitrogen atom, *i.e.*, ammonium groups. Compounds containing other polar groups, such as ether, amine, azo, nitro, ferrocenium, sulfoxide, sulfone, and disulfone may also be useful as solubility-suppressing components. Monomeric or polymeric

acetals having recurring acetal or ketal groups, monomeric or polymeric ortho carboxylic acid esters having at least one ortho carboxylic acid ester or amide group, enol ethers, N-acyliminocarbonates, cyclic acetals or ketals, β -ketoesters or β -ketoamides may also be useful as solubility-suppressing components. Compounds that
5 contain aromatic groups, such as phenyl, substituted phenyl such as *p*-methylphenyl, and naphthyl, are especially useful.

Compounds that contain a diazo group that are useful as dissolution inhibitor compounds include, for example, compounds that contain the *o*-diazonaphthoquinone moiety (*i.e.*, quinonediazides), preferably compounds that comprise an *o*-diazonaphtho-
10 quinone moiety attached to a ballasting moiety that has a molecular weight of at least 1500, but less than about 5000. Typically these compounds are prepared by the reaction of a 1,2-naphthoquinone diazide having a halogenosulfonyl group, typically a sulfonyl-chloride group, at the 4- or 5-position with a mono- or poly-hydroxyphenyl compound, such as mono- or poly-hydroxy benzophenone. Preferred reactive compounds are the
15 sulfonyl chloride or esters; the sulfonyl chlorides are most preferred. These compounds are discussed, for example, in Chapter 5 of Photoreactive Polymers: the Science and Technology of Resists, A. Reiser, Wiley, New York, 1989, pp. 178-225.

Useful compounds include, but are not limited to: 2,4-bis(2-diazo-1,2-dihydro-1-oxo-5-naphthalenesulfonyloxy)benzophenone; 2-di-azo-1,2-dihydro-1-oxo-5-naphthalene-
20 sulfonyloxy-2,2-bishydroxyphenylpropane monoester; the hexahydroxybenzophenone hexaester of 2-diazo-1,2-dihydro-1-oxo-5-naphthalenesulfonic acid; 2,2'-bis(2-diazo-1,2-dihydro-1-oxo-5-naphthalenesulfonyloxy)biphenyl; 2,2',4,4'-tetrakis(2-diazo-1,2-dihydro-1-oxo-5-naphthalenesulfonyloxy)biphenyl; 2,3,4-tris(2-diazo-1,2-dihydro-1-oxo-5-naphthalenesulfonyloxy)benzophenone; 2,4-bis(2-diazo-1,2-dihydro-1-oxo-4-naphtha-
25 lenesulfonyloxy)benzophenone; 2-diazo-1,2-dihydro-1-oxo-4-naphthalenesulfonyloxy-2,2-bishydroxyphenylpropane monoester; the hexahydroxybenzophenone hexaester of 2-diazo-1,2-dihydro-1-oxo-4-naphthalenesulfonic acid; 2,2'-bis(2-diazo-1,2-dihydro-1-oxo-4-naphthalenesulfonyloxy)biphenyl; 2,2',4,4'-tetrakis(2-diazo-1,2-dihydro-1-oxo-4-naphthalenesulfonyloxy)biphenyl; 2,3,4-tris(2-diazo-1,2-dihydro-1-oxo-4-naphthalene-
30 sulfonyloxy)benzophenone; and others known in the art, for example, those described in Mizutani, U.S. Pat No. 5,143,816.

The phenolic resin may be derivatized with an *o*-diazonaphthoquinone moiety.

Polymeric diazonaphthoquinone compounds include derivatized resins formed by the reaction of a reactive derivative that contains diazonaphthoquinone moiety and a polymeric material that contains a suitable reactive group, such as a hydroxyl or amino group. Suitable polymeric materials for forming these derivatized resins include the
5 novolac resins, resole resins, polyvinyl phenols, acrylate and methacrylate copolymers of hydroxy-containing monomers such as vinyl phenol and 2-hydroxyethyl methacrylate, polyvinyl alcohol, etc. Representative reactive derivatives include sulfonic and carboxylic acid, ester or amide derivatives of the diazonaphthoquinone moiety. Derivatization of phenolic resins with compounds that contain the diazonaphthoquinone
10 moiety is well known in the art and is described, for example, in West, U.S. Pat. Nos. 5,705,308, and 5,705,322. An example of a resin derivatized with a compound that comprises a diazonaphthoquinone moiety is P-3000, a naphthoquinone diazide of a pyrogallol/acetone resin (PCAS, France). These derivatized polymeric materials can act as both the second polymeric material and a solubility-suppressing component. They
15 can be used alone in the top layer, or they can be combined with other polymeric materials and/or solubility-suppressing components.

Compounds that contain a positively charged (*i.e.*, quaternized) nitrogen atom useful as dissolution inhibitor compounds include, for example, tetraalkyl ammonium compounds, quinolinium compounds, benzothiazolium compounds, pyridinium
20 compounds, and imidazolium compounds. Representative tetraalkyl ammonium dissolution inhibitor compounds include tetrapropyl ammonium bromide; tetraethyl ammonium bromide; tetrapropyl ammonium chloride; and trimethylalkyl ammonium chlorides and trimethylalkyl ammonium bromides, such as trimethyloctyl ammonium bromide and trimethyldecyl ammonium chloride. Representative triarylmethane dyes
25 dissolution inhibitor compounds include ethyl violet, crystal violet, malachite green, brilliant green, Victoria blue B, Victoria blue R, and Victoria pure blue BO.

Quaternized heterocyclic compounds are useful as dissolution inhibitors. Representative imidazolium compounds include Monazoline C, Monazoline O, Monazoline CY, and Monazoline T, all of which are manufactured by Mona Industries.
30 Representative quinolinium dissolution inhibitor compounds include 1-ethyl-2-methyl quinolinium iodide, 1-ethyl-4-methyl quinolinium iodide and cyanine dyes that comprise a quinolinium moiety such as Quinoldine Blue. Representative benzothiazolium

compounds include 3-ethyl-2(3H)-benzothiazolylidene)-2-methyl-1-(propenyl)benzothiazolium cationic dyes and 3-ethyl-2-methyl benzothiazolium iodide. Suitable pyridinium dissolution inhibitor compounds include cetyl pyridinium bromide and ethyl viologen dications.

5 Diazonium salts are useful as dissolution inhibitor compounds and include, for example, substituted and unsubstituted diphenylamine diazonium salts, such as methoxy-substituted diphenylamine diazonium hexafluoroborates. These compounds are particularly useful in non-preheat plates.

Representative sulfonic acid esters useful as dissolution inhibitor compounds
10 include ethyl benzene sulfonate, *n*-hexyl benzene sulfonate, ethyl *p*-toluene sulfonate, *t*-butyl *p*-toluene sulfonate, and phenyl *p*-toluene sulfonate. Representative phosphate esters include trimethyl phosphate, triethyl phosphate, and tricresyl phosphate. Useful sulfones include those with aromatic groups, such as diphenyl sulfone. Useful amines include those with aromatic groups, such as diphenyl amine and triphenyl amine.

15 Keto containing compounds useful as dissolution inhibitor compounds include, for example, aldehydes; ketones, especially aromatic ketones; and carboxylic acid esters. Representative aromatic ketones include xanthone, flavanone, flavone, 2,3-diphenyl-1-indenone, 1'-(2'-acetonaphthonyl)benzoate, α - and β -naphthoflavone, 2,6-diphenyl-4H-pyran-4-one and 2,6-diphenyl-4H-thiopyran-4-one. Representative carboxylic acid esters
20 include ethyl benzoate, *n*-heptyl benzoate, phenyl benzoate.

A preferred group of dissolution inhibitor compounds are those that are also dyes, especially triarylmethane dyes such as ethyl violet. These compounds can also act as contrast dyes, which distinguishes the unimaged regions from the imaged regions in the developed imageable element.

25 When a dissolution inhibitor compound is present in the top layer, its amount can vary widely, but generally it is at least about 0.1 wt%, typically about 0.5 wt% to about 30 wt%, preferably about 1 wt% to 15 wt%, based on the total dry composition weight of the layer.

Alternatively, or additionally, the second polymeric material can comprise polar
30 groups that act as acceptor sites for hydrogen bonding with the hydroxy groups present in the polymeric material and, thus, act as a solubility-suppressing component. Using methods well known to those skilled in the art, a portion of the polymeric material

hydroxyl groups can be derivatized to introduce polar groups, for example carboxylic acid esters, such as benzoate esters; phosphate esters; ethers, such as phenyl ethers; and sulfonic acid esters, such as methyl sulfonates, phenyl sulfonates, *p*-toluene sulfonates (tosylates), and *p*-bromophenyl sulfonates (brosylates).

5 Derivatization of the hydroxyl groups of the polymeric material increases its molecular weight and reduces the number of hydroxyl groups, typically reducing both the solubility and the rate of dissolution of the polymeric material in the developer. Although it is important that the level of derivitization be high enough that the polymeric material acts as a solubility-suppressing component, it should not be so high that, 10 following thermal imaging, the polymeric material is not soluble in the developer. Although the degree of derivitization required will depend on the nature of the polymeric material and the nature of the moiety containing the polar groups introduced into the polymeric material, typically about 0.5 mol% to about 5 mol%, preferably about 1 mol% to about 3 mol%, of the hydroxyl groups will be derivatized. These derivatized 15 polymeric materials can act as both the second polymeric material and a solubility-suppressing component. They can be used alone in the top layer, or they can be combined with other polymeric materials and/or solubility-suppressing components.

One preferred group of polymeric materials that comprise polar groups and function as solubility-suppressing components are derivatized phenolic polymeric 20 materials in which a portion of the phenolic hydroxyl groups have been converted to sulfonic acid esters, preferably phenyl sulfonates or *p*-toluene sulfonates. Derivatization can be carried by reaction of the polymeric material with, for example, a sulfonyl chloride such as *p*-toluene sulfonyl chloride in the presence of a base such as a tertiary amine. A preferred polymeric material is a derivatized novolac resin in which about 1 25 mol% to 3 mol%, preferably about 1.5 mol% to about 2.5 mol%, of the hydroxyl groups have been converted to phenyl sulfonate or *p*-toluene sulfonate (tosyl) groups.

It will be appreciated by those skilled in the art that although phenolic polymers which have been derivatized with polar groups [*e.g.*, polymers in which some of the hydroxyl groups have been derivatized with sulfonic acid ester groups or with groups 30 that contain the diazonaphthoquinone moiety] are soluble in aqueous alkaline developer, a layer comprising or consisting essentially of one or more of these materials is "insoluble" in aqueous alkaline developer. This is because solubility and insolubility of

the layer are determined by the relative rates at which the imaged and unimaged regions of the layer are removed by the developer. Following imagewise thermal exposure of a layer comprising or consisting essentially of one or more of these derivatized phenolic polymeric materials, the exposed regions of the layer are removed by the aqueous

5 alkaline developer more rapidly than the unexposed regions. If the development step is carried out for an appropriate time, the exposed regions are removed and the unexposed regions remain, so that an image made up of the unexposed regions is formed. Hence the exposed regions are "removable" or "soluble" in the aqueous developer and the unexposed regions are "not removable" or "insoluble" in the aqueous alkaline developer.

10 The solubility-suppressing components are believed not to be sensitive, *i.e.* photoreactive, themselves to radiation in the range of about 600 nm to about 800 nm and radiation in the range of about 800 nm to about 1200 nm, the range typically used for imaging a thermally imageable element.

If radiation is to be used for imaging and it is to be absorbed in the underlayer
15 (*i.e.*, the underlayer comprises an imaging radiation absorber), the solubility-suppressing component preferably should not absorb a significant amount of the imaging radiation. The imaging radiation should pass through the top layer so that it is absorbed by the absorber in the underlying underlayer. Thus, unless absorption of imaging radiation by the top layer is desired, when a dye is used as the solubility-suppressing component, it
20 should not absorb a significantly at the imaging wavelength. Preferably, the imaging radiation absorber absorbs more strongly in the range of about 800 nm to about 1200 nm than it does in the visible (*i.e.*, about 380 nm to about 780 nm).

If absorption of radiation in the range of 600 nm to 1200 nm, or the range of 800 nm to 1200 nm, in the top layer is desired, an absorber, *i.e.* a photothermal conversion
25 material such as is described above, may be added to the top layer. When the underlayer contains a photothermal conversion material, the top layer may also contain a photothermal conversion material, which typically is the same infrared absorbing material used as the photothermal conversion material in the underlayer. When the underlayer comprises a negative-working, base soluble photosensitive composition, the
30 photothermal conversion material may be in the top layer, in the underlayer, or in both the top layer and the underlayer.

When a photothermal conversion material is present in the top layer, it may

comprise infrared absorber or dye bound to a phenolic material (*i.e.*, a phenolic material derivatized with an infrared absorber or infrared absorbing dye). If an appropriate infrared absorber or dye is selected, the derivatized polymeric material can act as the second polymeric material, the solubility-suppressing component, and/or the

5 photothermal conversion material.

The top layer may also comprise dye to aid in the visual inspection of the exposed and/or developed element. Printout dyes to distinguish the exposed regions from the unexposed regions during processing. Contrast dyes distinguish the unimaged regions from the imaged regions in the developed plate.

10 The top layer may also comprise a cellulose polymer or polymers to improve the resistance of the layer to blanket washes with, for example, petroleum ethers, glycols, glycol ethers, and branched alkanols, for example iso-propyl alcohol and 1-methoxypropan-2-ol. Preferably the top layer comprises a carboxylic acid containing cellulose polymer, such as cellulose acetate phthalate, cellulose acetate hydrogen
15 phthalate, and/or cellulose acetate trimellitate. Typically the cellulose polymer comprises 0.1% to 50% by weight, preferably 5% to 20% by weight, and more preferably 8% to 12% by weight of the top layer. The acid number for the cellulose polymer is typically 50-210, preferably 100-180.

The top layer and/or the underlayer may comprise Particulate material to
20 improve both the scratch resistance and presslife of the exposed and developed element. Typically, the particles have an average diameter about 0.5 μm and about 10 μm . Organic and/or inorganic particulate material may be used. Examples of organic particles are crosslinked polystyrene beads and polymethyl methacrylate beads. Non-crosslinked polymers such as polycarbonate and acrylonitrile-butadiene copolymers,
25 which form particles in situ during the drying process, are also useful in improving presslife of the exposed and developed elements. Inorganic particles include, for example, silica and alumina particles. The amounts of particles used can range from 0.5% to 30% of the coating weight of the layer, preferably is 5% to 15%.

Preparation of the Thermally Imageable Element

30 The thermally imageable element may be prepared by sequentially applying the underlayer over the hydrophilic surface of the hydrophilic substrate, and then applying the top layer over the underlayer using conventional coating or lamination methods.

However, it is important to avoid intermixing the underlayer and top layer.

The underlayer, or first layer, may be applied over the hydrophilic substrate by any conventional method. Typically the ingredients are dispersed or dissolved in a suitable coating solvent, and the resulting mixtures coated by conventional methods, such as spin coating, bar coating, gravure coating, or roller coating. The top layer, or second layer, may be applied over the underlayer, typically to the surface of the underlayer by any conventional method, such as those listed above. The term "solvent" includes mixtures of solvents, especially mixtures of organic solvents.

Selection of the solvents used to coat the underlayer and to coat the top layer will depend on the nature of the first polymeric material, the second polymeric material, and the other ingredients present in the layers. To prevent the underlayer from dissolving and mixing with the top layer when the top layer is coated over the underlayer, the top layer should be coated from a solvent in which the first polymeric material is essentially insoluble. Thus, the coating solvent for the top layer should be a solvent in which the second polymeric material is sufficiently soluble that the top layer can be formed and in which the first polymeric material is essentially insoluble. Although the solvents used depend on the nature of the polymeric materials, typically the first polymeric material will be soluble in more polar solvents and insoluble in less polar solvents so that the solvent used to coat the underlayer is more polar than the solvent used to coat the top layer. Consequently, the top layer can typically be coated from a conventional organic solvent such as toluene, 2-butanone, propyleneglycol acetate, *n*-butanol, *iso*-propyl alcohol, or butyl acetate. An intermediate drying step, *i.e.*, drying the underlayer to remove coating solvent before coating the top layer over it, may also be used to help prevent mixing of the layers.

The top layer may be coated as an aqueous dispersion to avoid dissolving the underlayer during the coating process. Alternatively, the underlayer, the top layer or both layers may be applied by conventional extrusion coating methods from a melt mixture of layer components. Typically, such a melt mixture contains no volatile organic solvents.

30

Imaging

Imaging of the imageable element produces an imaged element, which comprise a latent image of imaged and unimaged regions. Developing the exposed element to form

a developed element converts the latent image to an image by removing the exposed regions of the top layer and the underlayer, and exposing the hydrophilic surface of the underlying substrate. The element is positive working, in that the underlayer and top layers are removed in the exposed regions. The exposed regions become the non-ink
5 accepting regions.

While not being bound by any theory or explanation, it is believed that a thermally frangible complex is formed between the solubility-suppressing component and the polymeric material. When the element is heated, typically by imagewise thermal exposure, the thermally frangible complex breaks down. The developer penetrates the
10 exposed regions of the top layer much more rapidly than it penetrates the unexposed regions. The underlying regions of the underlayer are removed along with the exposed regions of the top layer, revealing the underlying hydrophilic surface of the substrate.

The thermally imageable element may be imaged with a laser or an array of lasers emitting modulated near infrared or infrared radiation in a wavelength region that
15 is absorbed by the element. Infrared radiation, especially infrared radiation in the range of about 800 nm to about 1200 nm, is typically used for imaging a thermally imageable element. Imaging is conveniently carried out with a laser emitting at about 830 nm or at about 1056 nm. Suitable commercially available imaging devices include image setters such as a Creo Trendsetter (available from the CREO Corp., British Columbia, Canada)
20 and a Gerber Crescent 42T (available from the Gerber Corporation).

Alternatively, the thermally imageable element may be imaged using a conventional apparatus containing a thermal printing head. An imaging apparatus suitable for use in conjunction with the imageable elements includes at least one thermal head but would usually include a thermal head array, such as a TDK Model No. LV5416
25 used in thermal fax machines and sublimation printers. When exposure is carried out with a thermal head, it is unnecessary that the element absorb infrared radiation. However, elements that absorb infrared radiation can be imaged with a thermal head.

In either case, the image signals are stored as a bitmap data file on a computer. Such files may be generated by a raster image processor (RIP) or other suitable means.
30 For example, a RIP can accept input data in page-description language, which defines all of the features required to be transferred onto the imageable element, or as a combination of page-description language and one or more image data files. The

bitmaps are constructed to define the hue of the color as well as screen frequencies and angles.

The developer may be any liquid or solution that can penetrate and dissolve both the exposed regions of the top layer and the underlying regions of the underlayer without substantially affecting the complimentary unexposed regions. While not being bound by any theory or explanation, it is believed that image discrimination in these systems is based on a kinetic effect. The exposed regions of the top layer dissolve more rapidly in the basic developer than the unexposed regions. Development is carried for a long enough time to dissolve the exposed regions of the top layer and the underlying regions of the underlayer in the developer, but not long enough to dissolve the unexposed regions of the top layer. Hence the exposed regions are described as being "soluble" in the developer because they dissolve more rapidly in the developer than the unexposed regions. However, it will be appreciated that, if the exposed element is developed for a long enough time, both the exposed and the unexposed regions will be dissolved.

Useful developers are aqueous solutions having a pH of about 7 or above. Preferred aqueous alkaline developers are those that have a pH between about 8 and about 13.5, typically at least about 11, preferably at least about 12. Wholly aqueous developers, *i.e.*, those that do not comprise an added organic solvent, are preferred. Useful developers include commercially available developers, such as PC3000, PC955, and PC9000, aqueous alkaline developers each available from Kodak Polychrome Graphics LLC.

Typically the developer is applied to the imaged element by rubbing or wiping the top layer with an applicator containing the developer. Alternatively, the imaged element may be brushed with the developer or the developer may be applied to the element by spraying the top layer with sufficient force to remove the exposed regions. In either instance, a developed element is produced.

The developed element, typically a lithographic printing plate or printing member, comprises (1) regions in which the underlayer and top layer have been removed revealing the underlying surface of the hydrophilic substrate, and (2) complimentary regions in which the underlayer and top layer have not been removed. The regions in which both the underlayer and top layer have not been removed are ink receptive and correspond to the regions that were not exposed during imaging.

If desired, a post-development baking step can be used to increase the run length of the plate. Baking can be carried out, for example, at about 220°C to about 240°C for about 7 to 10 minutes.

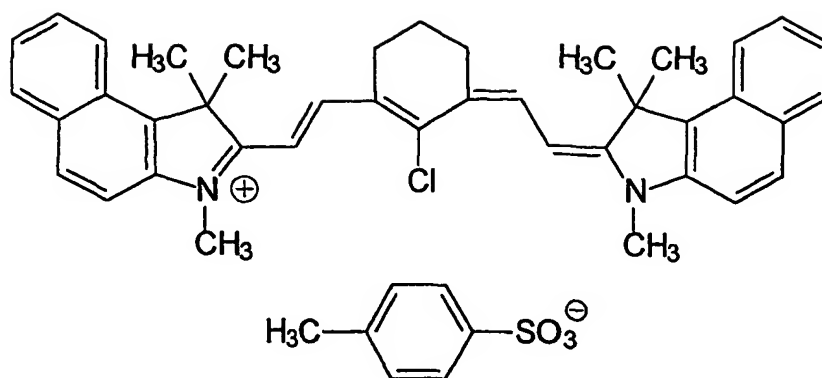
- If the underlayer comprises a negative-working, base soluble photosensitive composition, the developed element is exposed to actinic radiation. Any convenient source or sources of actinic radiation providing wavelengths in the region of the spectrum that overlap the absorption bands of the negative-working, base soluble photosensitive composition can be used to activate photoinsolubilization. By "actinic radiation" is meant any radiation that can induce photoinsolubilization in the underlayer.
- The radiation can be natural or artificial, monochromatic or polychromatic, incoherent or coherent. Conventional light sources include fluorescent lamps, mercury, metal additive and arc lamps. Coherent light sources are lasers, such as xenon, argon ion, and ionized neon lasers, as well as tunable dye lasers and the frequency doubled neodymium: YAG laser.
- The advantageous properties of the invention can be observed by reference to the following examples that illustrate, but do not limit, the invention.

EXAMPLES

Glossary

20	ACTILANE® 20	Acrylated aliphatic polyurethane resin (SNPE; Bergerac, France)
	ADS-830A	Infrared absorbing dye ($\lambda_{\max} = 830$ nm) (American Dye Source, Montreal, Canada)
	Copolymer 1	Copolymer of N-phenylmaleimide, methacrylamide, and methacrylic acid (50:35:15 mol%)
25	Copolymer 2	Copolymer of N-phenylmaleimide, methacrylamide, and methacrylic acid (45:35:20 mol%)
	Copolymer 3	Copolymer of N-phenylmaleimide, methacrylamide, and methacrylic acid (40:35:25 mol%)
30	DOWANOL® PM	Propylene glycol methyl ether
	EC2117	Infrared absorbing dye ($\lambda_{\max} = 830$ nm) (FEW, Wolfen, Germany)

Ethyl Violet	C.I. 42600; CAS 2390-59-2 (λ_{\max} = 596 nm) [$(p-(\text{CH}_3\text{CH}_2)_2\text{NC}_6\text{H}_4)_3\text{C}^+ \text{Cl}^-$]
GANTREZ® AN119	Linear methyl vinyl ether/maleic anhydride copolymer; specific viscosity of 0.1 to 0.5 (1% in 2-butanone at 25°C); molecular weight of 190,000 (ISP, New Jersey, USA)
5 Jagotex MA2814/3	Acrylic resin (Jaeger, Düsseldorf, Germany)
JONCRYL® 683	Styrene/acrylic copolymer (MW = 7,300) (S.C. Johnson, Wisconsin, USA)
Leuco crystal violet	CAS 603-48-5; [$(p-(\text{CH}_3)_2\text{NC}_6\text{H}_4)_3\text{CH}$]
10 LB744	Cresol novolac resin (Bakelite, Iserlohn- Letmathe, Germany)
Nega 107	Negative diazo resin derived from condensation of 3- methoxy-diphenylamine-4-diazonium sulfate and 4,4'-bis- methoxymethyldiphenylether, isolated as mesitylene sulfonate salt (Panchim, Lisses, France)
15 Novolac SPN 400	Novolac resin (Clariant, Wiesbaden, Germany)
PD 140	Novolac resin (Borden Chemical, Columbus, OH USA)
PMP234	Copolymer (40:50:10 wt%) of APK-234, acrylonitrile, and methacrylamide; APK-234 is a urea substituted monomer of the following structure: [$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}_2-\text{CH}_2\text{CH}_2-\text{NH}-\text{CO}-\text{NH}-p-\text{C}_6\text{H}_4-\text{OH}$]
20 PU Copolymer	Copolymer of N-(<i>p</i> -aminosulfonylphenyl)methacrylamide, acrylonitrile, and methyl methacrylate (34/24/42 mol% = 60.5/9.3/30.2 wt%)
25 SARTOMER® 355	Ditrimethylolpropane tetraacrylate (Cray Valley, Paris, France)
Triazine B	2,4-Bis(trichloromethyl)-6-(4-methoxy-1-naphthyl)-1,3,5- triazine (PCAS, France)
Triazine E	2,4-Bis(trichloromethyl)-6-((5-ethoxyethoxy)naphthyl)- 1,3,5-triazine (Panchim, Lisses, France)
30 Trump IR Dye	Infrared absorbing dye (λ_{\max} = 830 nm), same as EC2117 (Eastman Kodak, Rochester, NY, USA)



EC2117

5

EXAMPLE 1

This example describes the preparation of a tosylated novolac resin tosylated to 1.8 mol%. Dry novolac resin (120 g) is dissolved by stirring in acetone (325 g) in a 600 mL beaker and the solution cooled to about 10°C. *p*-Toluene sulfonyl chloride
 10 (3.56 g) is added over a period of about 1 min. Triethyl amine (2.09 g) is added at about 10°C over a period of about 1 hr and the reaction mixture stirred at ≤15°C for 1 hr. Acetic acid (1.36 g) is added at about 10°C over about 1 min and the reaction mixture stirred for about 15 min.

A mixture of 3.0 kg of ice and 3.0 kg of water is placed in a 7.5 L breaker.
 15 Acetic acid (5 g) is added with stirring and the mixture stirred at about 15°C for about 1 min. About 25% of the reaction mixture is added and the mixture stirred for about 20 min. The reaction mixture is allowed to settle for about 20 min and the supernatant decanted from the precipitate.

Water (about 1.9 Kg) is added to the precipitate and the resulting mixture stirred
 20 for 5 min at about 15°C. The precipitate is allowed to settle for 20 min and the supernatant decanted. The process is repeated with the remaining three portions of the reaction mixture. The precipitate is collected and dried to yield about 123 g of tosylated novolac resin in which about 1.8 mol% of the hydroxyl groups have been converted to tosyl groups.

25 By this procedure, a novolac resin tosylated to 1.8 mol% is prepared from a *m*-cresol/formaldehyde novolac resin from Schenectady Inter., Schenectady, NY, USA.

Example 2

Following the procedure of Example 1, a novolac resin tosylated to 1.8 mol% is prepared from a cresol/formaldehyde novolac resin (75:25 *m*-cresol/*p*-cresol) obtained from Borden Chemical, Columbus, OH, USA.

Example 3

This example describes the preparation of Copolymer 2. Methyl glycol (800 mL) was placed in a 1 L round-bottomed flask equipped with a stirrer, thermometer, nitrogen inlet and reflux condenser. Methacrylic acid (36.12 g), N-phenylmaleimide (165.4 g), and methacrylamide (62.5 g) added and dissolved with stirring. 2,2-Azobisisobutyronitrile (AIBN) (3.4 g) was added and the reaction mixture heated at 60°C with stirring for 22 hr. Then methanol was added, and the precipitated copolymer filtered, washed twice with methanol, and dried in the oven at 40°C for 2 days.

If the polymerization is carried out in 1,3-dioxolane, in some cases reprecipitation can be avoided. The monomers are soluble in 1,3-dioxolane, but the polymeric material is insoluble and precipitates during the reaction.

Example 4

Following the procedure of Example 3, methacrylic acid (27.1 g), N-phenylmaleimide (183.7 g), and methacrylamide (62.5 g) were reacted with AIBN (3.4 g) to form Copolymer 1.

Example 5

This example describes the preparation of Copolymer 3. Following the procedure of Example 3, methacrylic acid (55.74 g), N-phenylmaleimide (181.48 g), methacrylamide (77.13 g) were heated with AIBN (0.425 g) at 60°C with stirring for about 24 hr. Then about 5 L of methanol was added, and the precipitated copolymer filtered, washed twice with methanol, and dried in the oven at 40°C for 2 days.

Example 6

This example illustrates the preparation of N-(*p*-phenylsulfonamide)-substituted

(methyl vinyl ether/maleimide) copolymer, a polymeric material that incorporates an N-substituted cyclic imide moiety. A 20 wt% solution of GANTREZ® AN119 was prepared using anhydrous N-methylpyrrolidone (NMP). A sample of the solution (156 g) was placed in a beaker and dissolved in anhydrous NMP (300 g). Once dissolved, *p*-aminobenzenesulfonamide (34.46 g) was added and dissolved by stirring. Then, dimethylaminopyridine (0.2 g) was dissolved in the solution. After stirring for 45 minutes at ambient temperature, the solution was heated to 90-95°C by immersion in a hot water bath for 1 hr. The mixture was allowed to cool and left to stand overnight.

A 3 L beaker containing 2 L of distilled water containing 10 mL of concentrated hydrochloric acid was stirred. The reaction mixture was very slowly poured into the stirring water as a thin stream causing the desired product to precipitate as a tan-pink suspension. The mixture was stirred for 2 hr and then allowed to settle. The mixture was filtered and re-suspended in a further 2 L of water for 2 hr before filtering and drying in a fan oven overnight to form dark brown granules (48.4 g; 78.0% yield).

FTIR Analysis shows the presence of the imide C-N-C stretch showing that a cyclic imide is present in the produce. A very weak peak also shows the presence of N-H groups of an amide group suggesting the presence of a hydrolyzed or non-ring closed product present in a trace amount.

Other copolymers that incorporate an N-substituted cyclic imide moiety may be prepared by this general procedure. For example, *p*-aminophenol can be reacted with GANTREZ® AN119 copolymer to prepare a copolymer that incorporates an N-substituted cyclic imide moiety.

Example 7

Copolymer 1 (4.8 g) and EC2117 (0.2 g) were dissolved in 45 g of methyl lactate/methanol/dioxolane (15:42.5:42.5 wt%) mixture and coated onto a substrate to give a coating weight of 1.83 g/m². The substrate was an aluminum sheet that had been electrochemically grained, anodized, and coated with polyvinyl phosphonic acid. LB744 (4.85 g) and ethyl violet (0.15 g) were dissolved in 60 mL of a mixture of DOWANOL® PM glycol ether and acetone (70:30 wt%) and coated on top of the previous layer at a coating weight of 1.25 g/m². The thermally imageable element thus formed was dried at 92°C for 90 min.

The thermally imageable element was imaged with a laser diode emitting at 810 nm mounted on a rotating drum to form lines and solids regions. The imaged element was developed in GOLDSTAR™ DC developer (Kodak Polychrome Graphics LLC) to from a lithographic printing plate. The image areas had good resistance to the developer. The plate showed good developability in the imaged areas, giving a clean background and lines.

The plate has a soak loss of 44% when given a blanket wash in diacetone alcohol/water (80:20 wt%) and 38% in ethylene glycol monomethyl ether. For comparison, the Fuji FPU plate has soak losses of 85% and 14% in these washes, respectively.

A plate was prepared by this procedure was treated with Kodak Polychrome Graphics 243 Deletion Fluid. The image was removed in about 0.5 min. A similar plate was baked at 230°C for 8 min and then treated with the deletion fluid. The image was not removed after 8 min.

Example 8

Copolymer 2 (4.8 g) and EC2117 (0.2 g) were dissolved in 45 g of methyl lactate/methanol/dioxolane (15:42.5:42.5 wt%) mixture and coated onto the substrate described in Example 7 to give a coating weight of 1.62 g/m². The tosylated novolac produced in Example 1 (2.45 g) and ethyl violet (0.05 g) were dissolved in 25 mL of a mixture of DOWANOL® PM glycol ether and acetone (70:30 wt%) and coated on top of the previous layer at a coating weight of 1.12 g/m². The thermally imageable element thus formed was dried at 92°C for 90 min.

The thermally imageable element was imaged as described in Example 7 to form lines and solids regions. The imaged element was developed in GOLDSTAR™ DC developer to form a printing plate. A good image with a clean background was obtained. After baking as described in Example 7, the image was not removed by deletion fluid after 8 min.

Example 9

Copolymer 2 (4.8 g) and EC2117 (0.2 g) were dissolved in 45 g of methyl lactate/methanol/dioxolane (15:42.5:42.5 wt%) mixture and coated onto the substrate

described in Example 6 to give a coating weight of 1.62 g/m². The tosylated novolac produced in Example 2 (2.45 g) and ethyl violet (0.05 g) were dissolved in 25 mL of a mixture of DOWANOL® PM glycol ether and acetone (70:30 wt%) and coated on top of the previous layer at a coating weight of 0.99 g/m². The thermally imageable element thus formed was dried at 92°C for 90 min.

The element was imaged as described in Example 7 to form lines and solids regions. The imaged element was developed in the GOLDSTAR™ DC developer to form a printing plate. A good image with a clean background was obtained. After baking as described in Example 7, the image was not removed by deletion fluid after 8 min.

Example 10

PMP234 (2.4 g), EC2117 (0.1 g), and ethyl violet (0.05 g) were dissolved in 25 g of ethylene glycol monomethyl ether and coated onto the substrate described in Example 7 to give a coating weight of 1.90 g/m². The tosylated novolac produced in Example 2 (4.85 g), tetrapropyl ammonium bromide (0.2 g) and ethyl violet (0.10 g) were dissolved in 70 mL of 2-butanone and coated on top of the previous layer at a coating weight of 0.8 g/m². The thermally imageable element thus formed was dried at 92°C for 90 min.

The element was imaged as described in Example 7 to form lines and solids regions. The imaged element was developed in the PC 2000M developer (Kodak Polychrome Graphics). The imaged regions had good resistance to the developer. A good image with a clean background was obtained. The coating soak loss was 30% in a blanket wash of diacetone alcohol. After baking as described in Example 7, the image was not removed by deletion fluid after 8 min.

Example 11

This example illustrates the use of a mixture of polymeric materials in the underlayer. Copolymer 3 (3.75 g), PU copolymer (1.25 g), and ADS-830A (0.9 g) were dissolved in a 100 g of a methanol/dioxolane/methyl lactate mixture (43:43:14 wt%). The resulting coating solution was spin coated onto the lithographic substrate at a coating weight of 1.5 g/m² to produce a coated substrate.

Solvent resistance of the underlayer was measured in terms of soak loss in two different solvent mixtures. The soak loss was measured by measuring the weight change of a 1 dm² plate before soaking at room temperature and after soaking for a specific time and drying. Soak loss was calculated by dividing the weight loss by the total weight of the coating. The one-minute soak loss for the underlayer in the 80 wt% diacetone alcohol/20 wt% mixture was 32%. The one-minute soak loss in the 80% 2-butoxy-ethanol/20% water was 1%.

LB744 (4.85 g) and ethyl violet (0.15 g) were dissolved in a mixture of 20 g of 2-methoxypropanol and 40 g of toluene to produce a coating solution that was spin coated over the coated substrate at a coating weight of 1.2 g/m² to produce a thermally imageable element. The thermally imageable element was imagewise exposed on the Creo Trendsetter at a power setting of 8.5 W and a drum speed of 120 rpm. The imaged element was developed by wiping a soft pad soaked with developer 956. A good image was obtained.

15

Example 12

This example illustrates the improvement in properties that can be obtained by using an ultraviolet sensitive underlayer containing a diazo resin.

A coating solution was prepared by dissolving 2.13 g of a carboxy-functional polyvinylacetal prepared from maleic anhydride, 2-(N-methylamino)-acetaldehyde dimethyl acetal, and polyvinyl alcohol following the procedure of Preparation Example 11 of Baumann, U.S. Pat. No. 5,700,619, 2.13 g of Nega 107 negative diazo resin, and 0.15 g of Trump IR Dye in 50 mL of 2-methoxyethanol, methanol, and 2-butanone (35:25:40). The solution was coated onto a substrate described in Example 7 to give an ultraviolet sensitive underlayer having a coating weight of 1.40 g/m².

A novolac resin (PD 140) was tosylated to 3.0 mol%. The tosylated resin (2.5 g) was dissolved in a mixture of butyl acetate and *n*-butanol (90:10) and coated over the previous layer to give a top layer coating weight of 0.5 g/m². The resulting thermally imageable element was dried at 90°C for 10 min.

Two elements were imaged with a Creo Trendsetter at 185 rpm and 9.5 W and developed with the negative developer 956 from Kodak Polychrome Graphics. A good image with a clean background was obtained.

One of the two imaged and developed elements was flood exposed with ultraviolet radiation with a dose of 300 mJ/cm² using a SACK LCX3 5W radiation source. Each element was soaked in diacetone alcohol for 15 min. The ultraviolet exposed element had a weight loss of 26%, corresponding to the loss of the top layer.

5 The element that had not been exposed to ultraviolet weight had a weight loss of 96% indicating an almost complete loss of both layers.

Example 13

This example illustrates the improvement in properties that can be obtained by
10 using an ultraviolet sensitive underlayer containing a photopolymerizable composition.

A coating solution was prepared by dissolving 2.25 g of JONCRYL® 683 resin, 2.25 g of Jagotex MA2814/3, 4.20 g ACTILANE® 20, 0.80 g of SARTOMER® 355 polymerizable monomer, 0.60 g Triazine E, 0.2 of mercapto-3-triazol, 0.14 g leuco crystal violet, and 1.0 g of Trump IR Dye in 100 mL of a mixture of 2-methoxy-ethanol,
15 methanol, and methyl ethyl ketone (35:25:40). The solution was coated onto the substrate described in Example 7 to produce an ultraviolet sensitive underlayer having a coating weight of 2.0 g/m².

A novolac resin (PD 140) was tosylated to 10 mol%. The tosylated resin (1.5 g) and 0.5 g of Novolac SPN 400 was dissolved in a mixture of butyl acetate and *n*-butanol
20 (90:10) and coated over the underlayer to give a top layer having a coating weight of 0.5 g/m². The resulting thermally imageable element was dried at 90°C for 10 min.

Two elements were imaged with a Creo Trendsetter at 185 rpm and 9.5 W and developed with the positive developer 4000 from Kodak Polychrome Graphics. A good image with a clean background was obtained. One of the two imaged and developed
25 elements was flood exposed with ultraviolet radiation as described in Example 12. Each element was soaked in diacetone alcohol for 15 min. The ultraviolet exposed element had a weight loss of 30%, corresponding to the loss of the top layer. The element that had not been exposed to ultraviolet weight had a weight loss of 99% indicating an almost complete loss of both layers.

30 Having described the invention, we now claim the following and their equivalents.

CLAIMS

1. A thermally imageable element comprising, in order:
 - a) a substrate, the substrate having a hydrophilic surface;
 - 5 b) an underlayer over the hydrophilic surface, the underlayer comprising a first polymeric material; and
 - c) a top layer over the underlayer, the top layer comprising a second polymeric material;in which:
 - 10 the top layer is ink receptive;
 - the top layer is insoluble in aqueous alkaline developer;
 - the top layer comprises at least one solubility-suppressing component;
 - the underlayer comprises a photothermal conversion material;
 - the underlayer is soluble in aqueous alkaline developer; and
 - 15 the second polymeric material is soluble in aqueous alkaline developer.
2. The thermally imageable element of claim 1 in which the second polymeric material is soluble in at least one organic solvent in which the first polymeric material is insoluble.
- 20 3. The thermally imageable element of claim 1 or claim 2 in which the second polymeric material contains phenolic hydroxyl groups.
4. The thermally imageable element of any of claims 1 to 3 in which the
25 photothermal conversion material is an absorber that is soluble in the aqueous alkaline developer.
5. The thermally imageable element of any of claims 1 to 4 in which the underlayer absorbs radiation in the range of about 800 nm to about 1200 nm, and the top
30 layer does not absorb significantly in the range of about 800 nm to about 1200 nm.
6. The thermally imageable element of any of claims 1 to 5 in which the

second polymeric material is a novolac resin, a novolac resin functionalized with polar groups, or a mixture thereof.

7. The thermally imageable element of any of claims 1 to 6 in which the
5 solubility-suppressing component is a dissolution inhibitor compound.

8. The thermally imageable element of any of claim 7 in which the
dissolution inhibitor compound is a selected from the group consisting of compounds
that contain the *o*-diazonaphthoquinone moiety, ammonium compounds, triarylmethane
10 dyes, and sulfonate esters.

9. The thermally imageable element of any of claims 1 to 8 in which the
second polymeric material is a novolac resin, a novolac resin functionalized with polar
groups, or a mixture thereof.

15

10. The thermally imageable element of any of claims 1 to 9 in which the first
polymeric material contains at least one functional group selected from the group
consisting of carboxylic acid, N-substituted cyclic imide, and amide.

20 11. The thermally imageable element of claim 10 in which the first polymeric
material is a copolymer that contains carboxylic acid, N-substituted cyclic imide, and
amide functional groups.

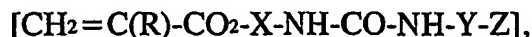
12. The thermally imageable element of claim 11 in which the first polymeric
25 material comprises about 25 to about 75 mol% of N-phenylmaleimide; about 10 to about
50 mol% of methacrylamide; and about 5 to about 30 mol% of methacrylic acid.

13. The thermally imageable element of claim 11 in which the first polymeric
material comprises about 35 to about 60 mol% of N-phenylmaleimide; about 15 to about
30 40 mol% of methacrylamide; and about 10 to about 30 mol% of methacrylic acid.

14. The thermally imageable element of any of claims 1 to 9 in which first

polymeric material is a copolymer that contains a pendent urea group.

15. The thermally imageable element of any of claims 1 to 13 in which the first polymeric material comprises about 20 to 80 wt% of one of more monomers
5 represented by the general formula:



in which R is -H or -CH₃; X is a bivalent linking group; Y is a substituted or
10 unsubstituted bivalent aromatic group; and Z is -OH, -COOH, or -SO₂NH₂.

16. The thermally imageable element of claim 15 in which R is CH₃; X is -(CH₂CH₂)-; Y is unsubstituted 1,4-phenylene; and Z is -OH.

- 15 17. The thermally imageable element of any of claims 1 to 9 in which the first polymeric material is a copolymer that contains a pendent sulfonamide group.

18. The thermally imageable element of claim 17 in which the first polymeric material contains about 10 to 90 mol% of a sulfonamide monomer unit; acrylonitrile or
20 methacrylonitrile; and methyl methacrylate or methyl acrylate.

19. The thermally imageable element of any of claims 1 to 18 in which the underlayer comprises a negative-working, base soluble photosensitive composition.

- 25 20. The thermally imageable element of claim 19 in which the negative-working, base soluble photosensitive composition is a photopolymerizable composition.

21. A thermally imageable element comprising, in order:
a) a substrate, the substrate having a hydrophilic surface;
30 b) an underlayer over the hydrophilic surface, the underlayer comprising a first polymeric material; and
c) a top layer over the underlayer, the top layer comprising a second polymeric material;

in which:

the element comprises a photothermal conversion material;

the top layer is ink receptive;

the top layer is insoluble in aqueous alkaline developer;

5 the top layer comprises at least one solubility-suppressing component;

the underlayer comprises a negative-working, base soluble photosensitive composition; and

the second polymeric material is soluble in aqueous alkaline developer.

10 22. The thermally imageable element of claim 21 in which the negative-working, base soluble photosensitive composition is a photopolymerizable composition.

23. A method for forming an image, the method comprising:

15 (1) thermally imaging the imageable element of any of claims 1 to 22 to form an imaged element; and

(2) developing the imaged element with an aqueous alkaline developer to form an imaged and developed element, the imaged and developed element comprising an image.

20 24. The method of claim 23 in which the underlayer comprises a negative-working, base soluble photosensitive composition, and the method additionally comprises the step of:

(3) exposing the imaged and developed element with actinic radiation after step (2).

25

25. An imaged and developed element, the element made by the method of claim 23 or claim 24.

INTERNATIONAL SEARCH REPORT

In International Application No

PCT/US 00/33605

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B41C1/10 B41N3/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B41C B41N B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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